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Relative Airborne Losses of Commercial 2,4-D Formulations from a Simulated Wheat Field

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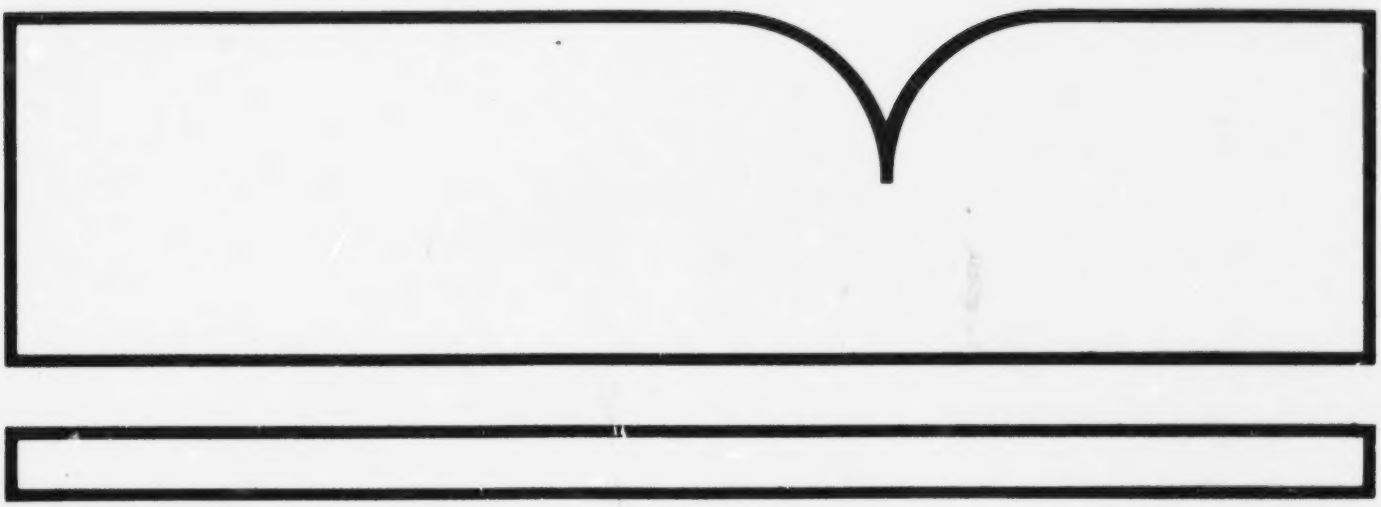

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Relative Airborne Losses of Commercial 2,4-D Formulations from a Simulated Wheat Field

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Abstract. The relative airborne losses of seven commercial 2,4-D (2,4-dichlorophenoxyacetic acid) formulations were evaluated in a simulated wheat field. The formulations tested were butyl ester, isooctyl ester, two propylene glycol butyl ether esters, ethanol/isopropyl amine, and two dimethyl amines. The butyl and isooctyl esters exhibited the greatest airborne losses, followed by the propylene glycol butyl ether esters. The amines were nearly nonvolatile. Two to 4 days after application, the 2,5-dichloro-4-hydroxyphenoxyacetic acid metabolite of 2,4-D predominated in all air samples. This material as well as the 2,4-D acid predominated in all plant samples with only traces of the parent esters observed. No extractable 2,4-D related residues were detected in the soil.

Wheat is the traditionally dominant crop in eastern Washington and northeastern Oregon. To obtain high crop yields, all cereal grains (including wheat) require intensive farm management including the use of agricultural chemicals. Typically applied as a commercially formulated ester or amine rather than as the parent acid, the herbicide 2,4-D (2,4-dichlorophenoxyacetic acid) in both agricultural and nonagricultural practices is one of the most commonly used chemicals for control of weedy species. Short-chain esters are classed as "high volatile," while longer chain esters or amines are considered "low volatile" varieties.

For three decades, grape production has expanded dramatically in eastern Washington. Although not as economically significant as wheat, grapes are a profitable crop. While wheat growers consider 2,4-D essential to successful wheat farming, grape growers feel that 2,4-D damages the vineyards. Since both wheat and grapes are grown in the same area (the Columbia Basin and Yakima Valley), it is not surprising that a substantial controversy has erupted over the use of 2,4-D. Sherwood *et al.* (1970) reported severe epinasty in concord grapes in a field study conducted at Iowa State University. They estimated average air concentrations of 2,4-D in the parts per billion (ppb) range. Continuous air monitoring was not performed; therefore, higher concentrations could have gone undetected. In a related 3-year greenhouse study of grapes in Iowa by Weigle *et al.* (1970), reduced yield and uneven ripening were attributed to the affects of 2,4-D at a concentration of 1 ppb. Whether grapes are sensitive to 2,4-D is not the issue, but rather the sources of the 2,4-D materials causing the damage.

Apparently 2,4-D is transported in the air from treated wheat fields into vineyards, resulting in damage to the grapes. Air monitoring at two sites in eastern Washington during 1963 showed 24-hr average concentrations of isopropyl, butyl, and isooctyl esters of 2,4-D ranging from undetectable to 3.1 $\mu g/m^3$ (Adams *et al.* 1964). Even though chemicals are added to reduce volatility, some scientists suspect that in certain weather conditions, both "low volatile" and "high volatile" materials may be transported substantial distances. In air monitoring surveys conducted in south-central Washington, Farwell *et al.* (1976) observed an average 2,4-D air concentration of 0.31 $\mu g/m^3$ in May 1973 and 0.84 $\mu g/m^3$ in 1974; most of the 2,4-D formulations were found to be "highly volatile" short chain esters (vapor pressure $\geq 10^{-5}$ mm Hg). Reisinger and Robinson (1976) postulate that weak frontal weather systems transport volatile 2,4-D

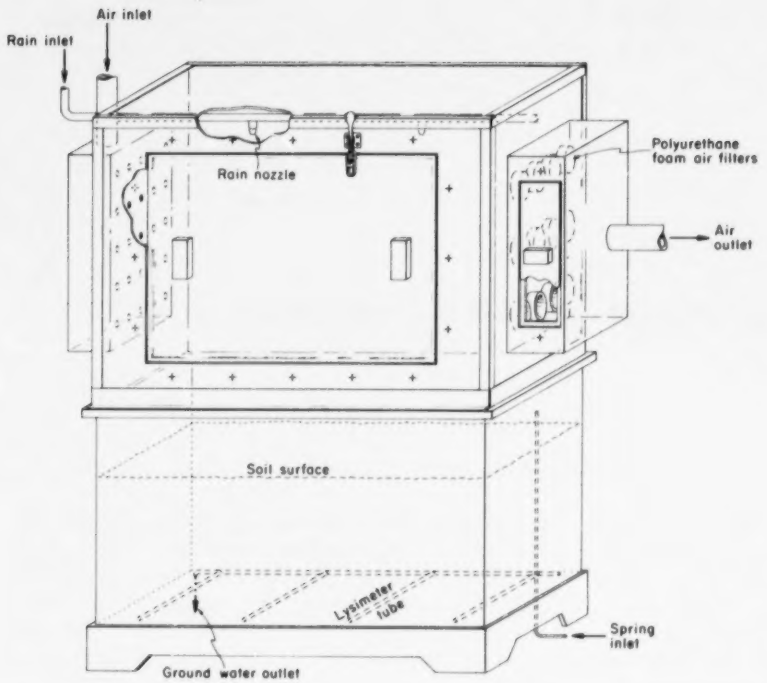

Fig. 1. Schematic of Terrestrial Microcosm Chamber (TMC-II)

compounds northward over long distances, while Decker and Hennessey (1977) suggest that the source of the problem is local use of 2,4-D combined with delays in implementing regulatory controls on 2,4-D applications. The State of Washington banned the use of high volatile 2,4-D formulations in May 1974.

Because of the controversy generated over the effects of 2,4-D on nontarget plants, this study was designed to use a simulated wheat field in a laboratory microcosm to examine the volatility of seven commercial formulations of 2,4-D and their relative losses by drift. Although the relative volatility of the various 2,4-D formulations is well known, this study attempted to verify these commercial formulations under simulated environmental conditions. The seven chemicals tested are commonly used in the wheat growing areas of eastern Washington and Oregon. The tests were conducted in the Terrestrial Microcosm Chamber (TMC-II) developed at the U.S. Environmental Protection Agency's research laboratory in Corvallis, Oregon.

Methods

Microcosm

The simulated ecosystem, the Terrestrial Microcosom Chamber (TMC-II) (Gile *et al.* 1982) consists of a glass, plexiglass, and polyethylene box, 1.25 ht. × 1.0 l. × 0.75 m in depth (Figure 1). From a single 1000 watt Sylvania Metalare lamp, each TMC-II received 38,000 lumens per m^2 at the soil surface during the 16-hr-day/ 8-hr-night cycle. Airflow through the microcosm was approximately 400 L/min, resulting in 37.6 air changes per hour. Calculated averages for the seven microcosms showed the daytime air temperature at 23°C ± 0.5, the daytime relative humidity at 55.5% ± 1.4%, the nighttime air temperature at 16°C ± 1°C, the soil temperature at 20.5°C ± 0.5°C, and the moisture content at 16.9% ± 0.4%. The soil was a typical Willamette Valley sandy loam (1.2% organic carbon, pH 6.43, water-holding capacity 22.9 @ 0.3 bar, particle density 2.59 μ/m^2). Nugaines White Winter Wheat (common head type) was supplied by the Washington State Department of Agriculture.

The result was a simulated wheat field which included a variety of wheat commonly used in both eastern Oregon and Washington, a soil generally similar to the natural situation and environmental conditions which would fall within the range of conditions experienced normally in the field during late spring.

Chemicals

The formulations of 2,4-D included two different brands of dimethylamine salt, an ethanol/isopropyl amine salt, two brands of propylene glycol butyl ether ester, an isooctyl ester, and a butyl ester. Based on their vapor pressure, these compounds can be divided into three classes: 1) the amines with vapor pressure $<10^{-7}$ m are classed as nonvolatile; 2) those compounds with a vapor pressure between 10^{-6} and 10^{-5} mm Hg (isooctyl and propylene glycol butyl ether ester) are considered slightly volatile; and 3) those formulations, such as the butyl ester, with a vapor pressure higher than 10^{-5} mm Hg are termed highly volatile (Farwell *et al.* 1976). All of the test chemicals were emulsifiable concentrates of technical grade available from commer-

cial sources with 2,4-D acid equivalents ranging from 26% for the butyl ester up to 46% for the isooctyl ester.

Experimental Procedures

Soil was added to each microcosm in two equal portions to a depth of 40 cm. Six L of water and a 24-hr compaction period followed each addition. The airflow was adjusted to 400 L/min and a 16-hr light cycle was established. After the systems had acclimated for 72 hr, the air and soil were monitored daily for temperature and moisture for the remainder of the study. Next, 160 wheat seeds were planted in each chamber, 8 cm apart in rows and covered with 1 cm of soil. After 26 days, the formulated 2,4-D (prepared as per the label) was sprayed on the plant foliage at a rate of 1.2 kg/ha (1 lb/A) of 2,4-D acid equivalent. To determine the distribution of 2,4-D within the ecosystem including its transport via air and metabolism, the air, plant, and soil samples were prepared and analyzed by high performance liquid chromatography (HPLC) techniques.

Organic extracts of air, plant, and soil samples were analyzed by HPLC in a Varian 5000 with a Vari-Chrom detector operating at 280 nm. A Micro-Pak C18 column was used with all samples. The solvent parameters were: reservoir A, water/2% acetic acid; reservoir B, acetronitrile/2% acetic acid. All samples were analyzed with isocratic solvents; the air samples used 50% reservoir B and the plant and soil used 30% reservoir B. The retention time for the air samples for the 2,4-D acid was approximately 3.2 min; for the plant samples, it was 5 min. The 2,5-dichloro-4-hydroxyphenoxyacetic acid had a retention time of 2 min for air samples and 4.3 min for plant samples. The retention time for the butyl ester was 4.5 min, for the isooctyl ester was 4 min, and for the propylene glycol butyl ether ester was 4.3 min for all samples tested. The amine salts were identified indirectly through acid determination.

Air Samples

The polyurethane filter plugs in the TMC-II exit air stream were extracted with acetone/hexane (1:1) for 24 hr, concentrated to 50 ml, and analyzed by HPLC. Samples were collected daily for the first seven days and then twice weekly for the remainder of the test.

Wheat Samples

Ten plants randomly selected were collected from each TMC and pooled for analysis at the end of the test. These samples were freeze-dried and then extracted for 72 hr in acetone. The extract was concentrated and analyzed by HPLC.

Soil Samples

Because experience indicated that 2,4-D rarely migrated deeper than 2 cm (residues below 2 cm were generally nonextractable), only the top 2 cm of soil from each TMC were used for soil samples. Samples, collected at the end of the test, were homogenized. After five 100-g subsamples were each extracted in hexanol/isopropanol (3:2) for 2 min, they were filtered through a Büchner funnel. After adding 50 ml of distilled water to each extract, both the aqueous and organic phases of the partitioned solution were analyzed by HPLC.

Table 1. Total 2,4-D materials in air

Chemical	2,4-D (mg)[a]	% of applied[b]
Butyl ester	26.1	17.5
Isooctyl ester	17.6	15.0
Propylene glycol Butyl ether ester[c]	6.3	5.1
Propylene glycol Butyl ether ester[c]	10.6	8.5
Ethanol/isopropyl amine	2.2	1.8
Dimethyl amine[c]	1.5	1.5
Dimethyl amine[c]	1.5	1.6

[a] Sum of parent ester and metabolites as determined by HPLC for all air samples throughout the experiment
[b] Based on percent of active ingredient in commercial formulation
[c] Different commercial products
Note: 2,5-dichloro-4-hydroxyphenoxyacetic acid dominated chromatography for all formulations 2 to 4 days after application

Results

Air

Volatility of the 2,4-D formulations decreased in the following order: butyl > isooctyl > propylene glycol butyl ether ester > ethanol/isopropyl amine > dimethyl amine (Table 1). The results found with each of these formulations is discussed below.

Butyl ester: Only four hr after application, this formulation resulted in an air concentration of 140 ng/L (Figure 2), which is a high initial loss rate. Being a short-lived phenomenon, the concentration declined to 2.16 ng/L within 48 hr. Through the 4th day, the ester was the major portion of the material detected and then the metabolite 2,5-dichloro-4-hydroxyphenoxyacetic acid became predominant. Although the detection limit for the ester was 1 μg/ml, the limit for the metabolite and acid was 3 μg/L. None of the samples contained detectable concentrations of 2,4-D.

Isooctyl ester: As with the butyl ester, the isooctyl ester exhibited a fairly high initial loss rate (24.5 ng/L at 4 hr sampling; Figure 2). Two days after application, the concentration of isooctyl exceeded that of the butyl ester. The parent ester remained the predominant component through the 5th day, with the hydroxy metabolite dominating thereafter. Again, no acid was observed. The isooctyl ester could not be detected at concentrations below 5 μg/L, while the detection limit for the metabolite and the acid was 3 μg/L. Similar amounts were recovered from the two ecosystems (Table 1; 17.5%—15%).

Propylene glycol butyl ether esters: The two products containing this ester had similar loss rates and overall loss (Figure 2; Table 1). The ester appeared in the first chromatographic peak, while the hydroxy metabolite appeared on the second day. Compared to the other formulations tested, these esters are in the midrange of volatility. Detection limits were the same as those indicated for the isooctyl ester.

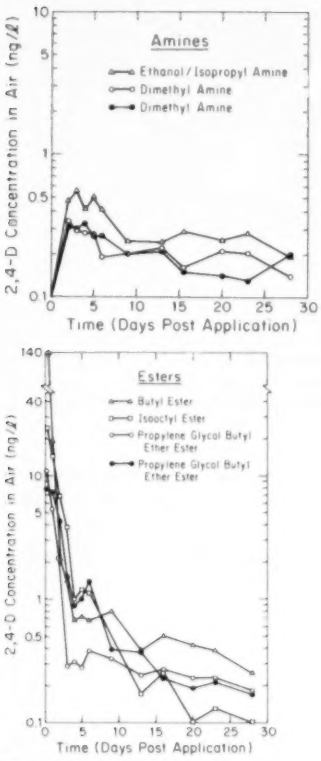

Fig. 2. Concentration of 2,4-D materials in air

Ethanol/isopropyl amine and dimethylamine salt: Throughout the study, the amines had low loss rates (Figure 2b). The amines were not detected until the second day, at which time the hydroxy metabolite appeared until the end of the test. Since these formulations were in the form of a salt, direct analysis by HPLC for the amine was not possible. The air filters were first extracted to remove any acid or metabolite, then acidified and extracted again to analyze for the amine. Acid detected in the final extract was assumed to be acidified amine.

Wheat/Soil

Analysis of wheat tissue in all systems (28 days after 2,4-D application) revealed a predominance of either the 2,4-D acid or the 2,5-dichloro-4-hydroxyphenoxyacetic acid metabolite (Table 2). The parent ester was observed in each of the three different ester formulations, but the amines were not analyzed for the parent formulation.

No extractable 2,4-D related material was detected in any of the soil samples for any formulation.

To avoid disturbance to the systems, neither wheat nor soil samples were collected prior to termination of the experiment. Therefore, no data on initial concentrations are available.

Discussion

Air

Although the relative volatility of the various 2,4-D formulations is well known, this study was conducted to verify the volatility of the commercial products, using simulated environmental conditions. Mullison and Hummer (1949) used bean and tomato plants to determine the relative volatility of various esters. They found that as the length of the alkyl ester side chain increases, volatility decreases. The data collected in this study tend to support that observation (Table 1). What may be of greater importance in determining long-term effects are the relative roles of drift and volatilization during and shortly after the spray operation vs the continued volatilization of the chemical from the site of application throughout the growing season. Because of the aerial spraying techniques commonly used with 2,4-D applications, one would expect higher losses near the time of application as was observed in our study. This in conjunction with our observation that the non-phytotoxic 2,4-D metabolite (2,5-dichloro-4-hydroxyphenoxyacetic acid) predominated in the air samples 2 to 4 days after application tends to minimize the problem of long-term effects from highly volatile formulations.

Table 2. 2,4-D materials in wheat[a] (μg/g)

Chemical	2,5-dichloro-4-hydroxy phenoxyacetic Acid	2,4-D acid	Parent formulation
Butyl ester	37.9	65.1	2.7
Isooctyl ester	40.7	40.7	2.0
Propylene glycol butyl ether ester[b]	23.2	23.3	trace[c]
Propylene glycol butyl ether ester[b]	34.0	27.4	trace
Ethanol/Isopropyl amine	22.6	28.5	ND[d]
Dimethyl amine[b]	20.9	39.5	ND
Dimethyl amine[b]	21.9	43.8	ND

[a] Each sample represents 10% (fresh weight) of total plant tissue from an ecosystem
[b] Different commercial products
[c] Detectable but not quantifiable
[d] Detection limits, 10 μg/ml

Wheat/Soil

It is generally accepted that both esters and salts of 2,4-D are rapidly hydrolyzed by plants, with rates affected primarily by plant species, climate and type of application. Klingman *et al.* (1966) observed rapid hydrolysis of both butyl and isooctyl esters by bluegrass within ½ hr after application. Morton *et al.* (1967) reported approximately 92% conversion of butoxyethyl ester and amine formulations to free acid by forage crops within 1 hr of application.

The hydroxylation of 2,4-D varies both qualitatively and quantitatively. While many of the metabolites in our study were not identified, the presence of the 2,5-dichloro-4-hydroxyphenoxyacetic acid supports earlier observations by Fleeker and Steen (1971) of the formation of both 2,3- and 2,5-dichloro-4-hydroxyphenoxyacetic acid by several weedy species. In addition, Montgomery *et al.* (1971) observed the same products in bean, bluegrass, and corn with the 2,5- predominating. Therefore, it is not surprising that this compound was the major material detected in the wheat.

Volatilization of 2,4-D materials from the soil is unlikely. Previous experience (Gile 1982) with ^{14}C labeled butyl ester indicated that the 2,4-D related materials in the soil were found in the top 2 cm and could not be extracted with techniques used in this laboratory.

In this experiment, there was little mass flow of water through the soil column. An average of 90 L was added to each TMC over the approximate 30 day period following 2,4-D application. During that same period, the leachate removed averaged less than 3 L total for any TMC. With a foliar application such as in our experiments, contamination of the soil is primarily the result of washoff. Since plants hydrolyze the esters to the acid, one would expect the acid not necessarily the formulation to be the primary form reaching the soil. With minimal water movement as we observed, the acid is probably converted to a less soluble form and hence remains in the upper soil layer. While 2,4-D materials in the soil could not be characterized by chromatrography, it is likely that all material was present as a metabolic or degradation product of the 2,4-D acid, since the acid breaks down in 4 to 6 weeks under normal growing conditions (Mullison 1972) which bracket the length of our tests (28 days).

Conclusions

The TMC-II studies showed that the 2,4-D esters examined have higher volatilization rates than the 2,4-D amines. Most of the 2,4-D related material is lost to the atmosphere within 2 to 4 days after application and is therefore probably related to spray drift and/or volatilization. While the butyl and isooctyl ester exhibited the highest loss rates, the parent ester was only minimally present in the air samples 2 to 4 days after application.

These findings suggest that the use of moderate or high volatile 2,4-D formulations could result in air concentrations that will produce damage to nontarget crops in the vicinity of a spraying site either during or shortly after 2,4-D application. While parent formulation could have been present but below our detection limits, continued release of the phytotoxic parent compound seems unlikely given the hydrolytic activity of plants in general as supported by our observations as well as the observations cited from the literature.

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